

Status Quo and Prospects of Development of Chemical and Sorption Heat Engines in the Russian Federation and the Republic of Belarus

Yu. I. Aristov^a, L. L. Vasilyev^b, V. E. Nakoryakov^c

^a The G.K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

^b The A.V. Lykov Institute of Thermo- and Mass Exchange, National Academy of Sciences of Belarus, ul. P. Brovki 15, Belarus

^c The S.S. Kutateladze Institute of Thermophysics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

Abstract—This paper examines basic principles of the operation of chemical and adsorption heat engines and their advantages and new aspects and reviews the status quo of sorption technologies in different countries and their use in Russia and in the Republic of Belarus.

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INTRODUCTION

For a long time, the main criterion in evaluation of a heat device was its efficiency, the limiting value of which for a heat engine doing work was determined by Carnot in 1824 [1]. In a similar way, it is possible to find out the limiting efficiency of the work of a heat pump or refrigerator (see below), which is the aim of the creators of these engines. The important practical criteria of the work of heat engines enumerated in [2] include the maximum efficiency at preset capital investments, the minimum self-cost at the preset efficiency, the best compliance of the properties of the working liquid with the specified output parameters, high reliability, low operation costs, etc.

However, recently quite new criteria have appeared that have substantially changed the evaluation of the work of heat devices. In the first revolution, it is an attempt to determine how much the device affects the natural environment. The reason for which these criteria are used is the concern of the world community with increased pollution with “greenhouse” gases (GG), which stimulated adoption of measures on stabilization and reduction of such processes. Measures formulated in the Montreal and Kyoto protocols amount mainly to regulation of GG emissions and taxes and quotas on emissions. It is clear already that the measures being adopted not only have ecological and economic consequences but can stimulate the development and application of a particular technology. Thus, serious constraints introduced on radical reduction of freon emissions are a real incentive to give up the use of freons in cooling and heating systems. On the one hand, this stimulates the development of compression heat engines (CHE) in which natural working bodies are used. On the other, a “niche” is opened for chemical

and sorption heat engines (ChHE and SHE) that may be important in the reduction of GG emissions. The use of these devices allows considerable economy of organic fuel due to the use of heat waste from the power system, various industrial productions, housing and utilities, and natural sources of low temperature heat.

We examine here technological, energy-related, and environmental aspects in the use of ChHE and SHE in the Russian Federation (RF) and the Republic of Belarus (RB). The basic principles and the status quo of these technologies in the RF and RB are compared to those at the world level with account of their climate and sources of thermal energy. Emphasis is made on those lines of science and technology in which studies performed in the RF and RB are at the world level or ahead of it. This analysis seems to be well to the point in view of the major restructuring to be performed in the heating energy of these countries and the high investments associated with it [3], part of which can be spent on the development of chemical and sorption heat engines.

1. CHEMICAL AND ADSORPTION HEAT ENGINES: BASIC PRINCIPLES, EFFICIENCY, AND WORKING PAIRS

Chemical and adsorption heat engines are considered now as a real alternative to compression devices. Their advantage is that they do not need electric power; heat that is at the moment not used, including that with low temperature potential, is enough for their operation. The first chemical heat pump was made by Faraday on the basis of the work pair $\text{NH}_3\text{--AgCl}$ in 1824 [4], i.e., much earlier than the first compression heat engine (1856/57, P. von Rittinger, Austria [5]). At

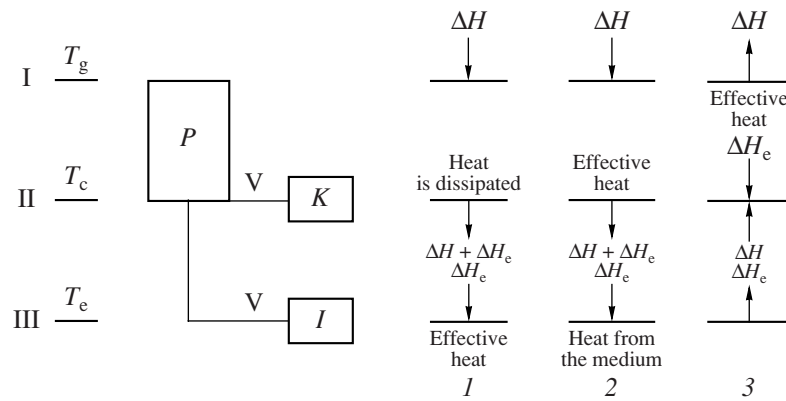


Fig. 1. Principle of the operation of the chemical (sorption) heat engine.

present, practical application of ChHE and SHE is getting ever more popular (see, for example, [6–8]).

A classical heat engine consumes heat Q_1 from a thermostat with a higher temperature T_1 and gives out heat Q_2 to a thermostat with low temperature T_2 and produces work $Q_1 - Q_2 = Q_1(1 - T_2/T_1)$. ChHE (SHE), on the other hand, uses and produces only heat energy and operates in the simplest case between three thermostats (I, II, and III) at high (T_g), intermediate (T_c), and low (T_e) temperatures (Fig. 1). These devices can transform heat energy by working in three modes (Fig. 1): cooling 1, heating 2, and increasing the temperature potential 3.

The simplest ChHE consists of the reactor P, evaporator I, and condenser K, which exchange vapor of the working liquid V and are coupled with thermostats I–III

(Fig. 1). In the reactor, the chemical reaction proceeds between compounds of nonvolatile S (sorbent) and volatile V (sorbate):



i.e., transformation of heat to chemical energy takes place. The evaporator is a source of volatile substance V in the reaction of formation of compound SV, and, in the device K, this substance is condensed after decomposition SV. Some examples of the reaction (1) are given in Table 1 (as the volatile compounds water, methanol, ethanol, and ammonia are considered). Since the chemical compound (complex) SV and condensate LV are pure phases, the pressure P of the component V in the reactor and condenser depends only on the temperature (monovariant equilibrium) and not on the conversion degree (the concentration V in the bound state).

Table 1. The values of the temperatures T_e , T_c , and T_g providing the reversibility of the refrigeration cycle CHE for different chemical reactions and the limit efficiency of the cycle

Reaction	T_e , °C	T_c , °C	T_g , °C	COP	$\Delta H_e/\Delta H$
$\text{BaCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	5	28	50	0.82	0.89
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O} \rightleftharpoons \text{CaCl}_2 \cdot 4\text{H}_2\text{O}$	5	35	67	0.87	0.85
$\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgCl}_2 \cdot \text{H}_2\text{O}$	20	134.0	267.7	0.65	0.64
$\text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} = \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$	20	70.8	120.3	0.72	0.73
$\text{SrBr}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O} \rightleftharpoons \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	5	44.1	72.5	0.59	0.61
$\text{SrBr}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O} \rightleftharpoons \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	10	47.9	77.3	0.62	0.61
$\text{MgO} + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2$	20	186	367	0.51	0.50
$\text{BaCl}_2 + 8\text{NH}_3 \rightleftharpoons \text{BaCl}_2 \cdot 8\text{NH}_3$	–20	26.7	65.8	0.63	0.62
$\text{BaCl}_2 + 8\text{NH}_3 \rightleftharpoons \text{BaCl}_2 \cdot 8\text{NH}_3$	–5	39.9	76.4	0.62	0.62
$\text{CaCl}_2 \cdot 4\text{NH}_3 + 4\text{NH}_3 \rightleftharpoons \text{CaCl}_2 \cdot 8\text{NH}_3$	–20	45.6	100.9	0.57	0.57
$\text{CaCl}_2 \cdot 4\text{NH}_3 + 4\text{NH}_3 \rightleftharpoons \text{CaCl}_2 \cdot 8\text{NH}_3$	–5	58.8	111.3	0.56	0.56
$\text{CaCl}_2 + 2\text{CH}_3\text{OH} \rightleftharpoons \text{CaCl}_2 \cdot 2\text{CH}_3\text{OH}$	–40	21.0	90.6	0.73	0.72
$\text{CaCl}_2 + 2\text{CH}_3\text{OH} \rightleftharpoons \text{CaCl}_2 \cdot 2\text{CH}_3\text{OH}$	–20.5	43.1	116.1	0.74	0.72
$\text{CaCl}_2 + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CaCl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$	21	57.6	94.6	0.81	0.83
$\text{CaCl}_2 \cdot \text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CaCl}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$	21	45.5	70.1	0.79	0.81

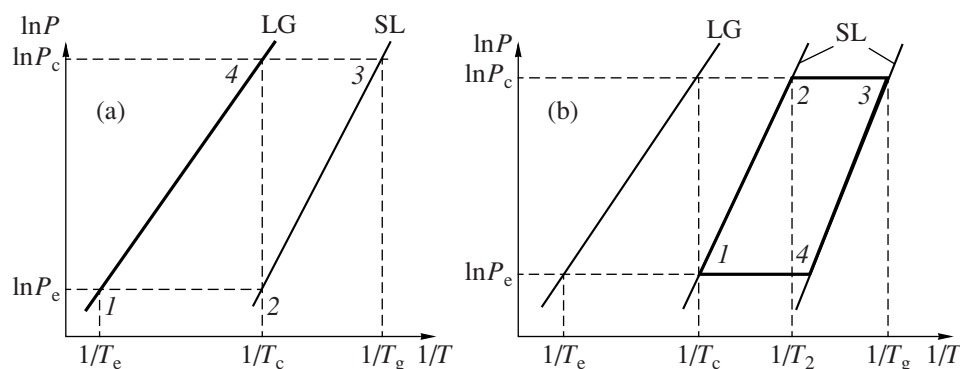


Fig. 2. Three-temperature cycle for chemical (a) and adsorption (b) heat engines.

These relationships, i.e., curves SL (solid–liquid) and LG (liquid–gas) in Fig. 2a, are usually described by equations [9]:

$$\ln P = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \quad (2)$$

$$\ln P = -\frac{\Delta H_e}{RT} + \frac{\Delta S_e}{R}, \quad (3)$$

where ΔH^0 and ΔS^0 are changes of the standard enthalpy and entropy in the formation of SV, and ΔH_e and ΔS_e are changes of the enthalpy and entropy in evaporation of V. Equations (2) and (3) are integral forms of the Vant–Hoff and Clapeyron–Clausius equations.

As mentioned, ChHE can operate both as a refrigerator (mode 1 in Fig. 1) and as a heater (mode 2). At the *regeneration stage*, which is common for these modes, heat from an outside source that is at the temperature T_g is supplied to the reactor, which is coupled with a condenser with temperature $T_c < T_g$. The equilibrium pressure of compound V in the reactor is by an infinitely small value higher than in the condenser, so this compound that has been formed in the decomposition of complex SV in the reactor is transmitted to the condenser where it is condensed at the temperature T_c . In the reactor, the heat ΔH is absorbed, and, in the condenser, the heat ΔH_e is released, which either is used for heating (heater mode) or is dissipated to the environment (refrigerator mode). After regeneration, the ChHE begins to operate in one of these modes.

In the *refrigerator mode*, the environment is a thermostat at the temperature T_e , and the temperature T_c is the required temperature of the refrigerator, i.e., the temperature at which heat is separated from the user's device. The equilibrium pressure of compound V in the evaporator at the temperature T_e is by an infinitely small value higher than in the reactor at temperature T_c , so the evaporated compound V is transmitted to the reactor where it forms complex SV. The heat of its formation ΔH is dissipated to the environment, and, in the evapo-

rator, the heat ΔH_e , which is taken from the user's device creating the effect of refrigeration, is absorbed. The efficiency (or refrigerator coefficient) is calculated as

$$\eta_{\text{cool}} = \Delta H_e / \Delta H. \quad (4)$$

The system returns to the initial (before regeneration) state.

In the *mode of a heater* (mode 2 in Fig. 1), the thermostat at the temperature T_e is the environment, and the temperature T_c at which heat is transmitted to the user is to comply with heating (commonly $T_c \geq 40^\circ\text{C}$). The equilibrium pressure of compound V in the evaporator at the temperature T_e is by an infinitely small value larger than the pressure in the evaporator at the temperature T_c , so this compound formed in the evaporation is transmitted to the reactor where it forms SV (Fig. 2a). In the evaporator, the heat ΔH_e , which is taken from the environment, is absorbed, and, in the reactor, the heat ΔH used for heating is released. The result of this stage is “call over” of heat from the environment with a low temperature T_e , at which it is possible to consume heat free of charge, to the reactor with a higher temperature T_c , and the system returns to its initial state. For heating, the heat released in the reactor and condenser is used and the efficiency (amplification factor) is found as

$$\eta_{\text{heat}} = (\Delta H + \Delta H_e) / \Delta H = 1 + \eta_{\text{cool}} > 1. \quad (5)$$

In the *third mode*, heat is absorbed in equilibrium at the temperature T_c , and useful heat ΔH is released in the course of the reaction of the formation of complex SV at the high temperature T_g with the efficiency

$$\eta_{\text{tp}} = \Delta H / (\Delta H_e + \Delta H) < 1. \quad (6)$$

In the calculation of all the efficiencies, an usual assumption was made that the expenditures of heat on the change of the heat capacity of the system are equal to null; i.e., we either ignore the thermal mass of the system or assume the effective recuperation of heat in it. Even if the recuperation is not full or is entirely absent, the costs of heating the system are usually small compared to the heat of the chemical transformations,

so the use of the approximation is also justified in this case.

The maximum theoretical efficiency of a heat engine operating between three thermostats with temperatures T_e , T_c , and T_g was obtained in [3, 10–12] for cooling

$$\eta_{\text{cool}} = \left(\frac{1}{T_c} - \frac{1}{T_g} \right) / \left(\frac{1}{T_e} - \frac{1}{T_c} \right) \quad (7)$$

and heating

$$\eta_{\text{heat}} = \left(\frac{1}{T_e} - \frac{1}{T_g} \right) / \left(\frac{1}{T_e} - \frac{1}{T_c} \right). \quad (8)$$

Using the methods of these studies, it is easy to also find the efficiency for the mode of increasing the temperature potential

$$\eta_{\text{t.p.}} = \left(\frac{1}{T_e} - \frac{1}{T_c} \right) / \left(\frac{1}{T_e} - \frac{1}{T_g} \right). \quad (9)$$

Therefore, the general thermodynamical analysis of three-temperature (3T) heat cycles leads to expressions (7)–(9), in which the efficiency is a function of the three temperatures of the cycle and does not depend on the characteristics of the work pair sorbent S – sorbate V. Table 1 presents values of the temperatures T_e , T_c , and T_g providing reversibility of the refrigeration cycle of ChHE obtained directly from the experimental curves of the equilibrium for different chemical reactions and limiting efficiencies of the cycle calculated from equations (7) and (4). The analysis of the efficiency of concrete ChHE cycles with account for monovariant equilibria (2) and (3) leads to expressions (4)–(6), according to which the efficiency depends only on the relationship of the enthalpy of the evaporation and the chemical reaction, i.e., on the characteristics of the work pair S–V. It is possible to show [13] that, for the reversible SHE, these determinations are equivalent since the three temperatures of the CHE cycle are not independent variables but are bound by the Clapeyron–Clausius equation for the equilibrium of a pure liquid and by the Vant–Hoff equation for a chemical reaction. Other important consequences of this relationship are considered below. The comparison of the efficiencies of ChHE and SHE cycles without heat regeneration shows that, for the ChHE, the efficiency can reach the Carnot efficiency and, for the SHE, it is always smaller due to generation of entropy in transmission of heat to an adsorber (from an adsorber) at the finite difference of temperatures [11].

Another crucial characteristic of ChHE and SHE is the specific power W_{sp} , i.e., the relationship of the power W absorbed in the evaporator (for cooling) or released in the condenser and adsorber (for heating) to the mass m (or volume V) of the sorbent:

$$W_{\text{sp}} = W/m \quad (10)$$

or

$$W_{\text{sp}} = W/V. \quad (11)$$

This value also depends on the thermodynamical characteristics of reaction (1), such as the amount of sorbate exchanged in the cycle, and on the dynamical parameters of the device, first of all, on the total time of the cycle. The latter, in turn, is determined by the intensity of the heat- and mass transfer processes connected with each other (which is described in more detail below). The value of W_{sp} may have a crucial importance for such applications of SHE (ChHE) as air conditioning in a car [14, 15] and a locomotive driver's cab [16], production of ice on fishing boats [17], etc. In all three cases, the low temperature heat from the cooling system of the engine is excessive, so the coefficient of its performance (COP) for refrigeration is not very important. The primary task is the production of high specific power, since the space for the cooling device is limited [18]. In some works, the energy efficiency of ChHE and SHE is introduced [19], but this characteristic has not yet been widely applied.

The working pairs “sorbate–sorbent” (V–S). The choice of the working pair for ChHE and SHE is determined by the three above mentioned temperatures (Fig. 2b). For ChHE, also important is the temperature T_d at which there is decomposition of complex SV at the pressure of the volatile substance equal to its pressure in the condenser (P_c). For reversible ChHE temperatures T_e , T_c , and T_d cannot be selected arbitrarily; they are connected with each other through equilibrium equations (2) and (5) [4, 13] (Fig. 2a).

As sorbates, water, ammonia, and methanol are used. The merits of water are its high heat of evaporation and ecological purity and the drawbacks are its low pressure of vapor and high freezing point. The first factor substantially retards the dynamics of absorption–desorption, which imposes substantial constraints on the specific power and dimensions of the device. In addition, in this case, the requirements for the tightness of the system are higher and the effect of even a small amount of residual gases may turn out as substantial.

Ammonia has a low freezing temperature and high pressure, but less than the water evaporation heat, and methanol is characterized by intermediate values of these characteristics. There are some works where as sorbates CO_2 [20], $\text{C}_2\text{H}_5\text{OH}$ [21], CH_3NH_2 [22], HFC 134a [23], and other substances are taken, but they are not common. Water is used usually in systems of air conditioning ($T_e = 5\text{--}15^\circ\text{C}$), methanol for air conditioning and producing ice ($T_e = -5\text{--}0^\circ\text{C}$), and ammonia also for major freezing.

After the sorbate and cycle are determined, it is necessary to select the sorbent optimal for the given cycle. The reviews [24–34] are devoted to discussion of work pairs that are suitable for different applications. At present, the following work pairs are mainly used:

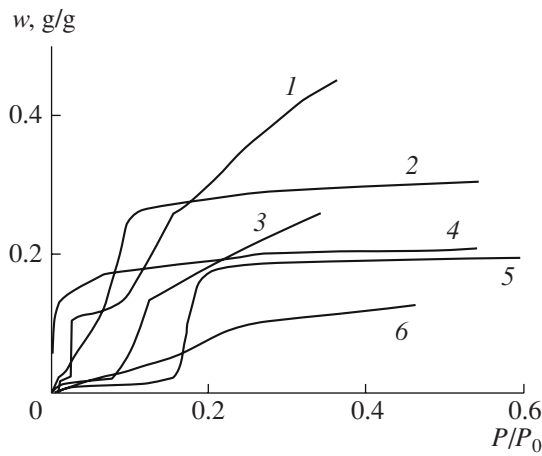


Fig. 3. Isotherms of water adsorption on CCB-1K (1), FAM-Z02 (2), CCB-5K (3), zeolite 13X (4), FAM-Z01 (5), and silica gel Fuji Davison RD (6).

for absorption heat engines (AbHE), ammonia–water and water–lithium bromide;

for adsorption heat engines (AdHE), zeolite–water, silica gel–water, coal–methanol, and coal–ammonia; and

for ChHE, chlorides of metals–ammonia and calcium chloride–methanol.

Substances used as solid sorbents are products of mass production (mostly for the needs of the chemical industry), so they are accessible, cheap, fairly well known, and nontoxic. Synthetic (3A, 4A, 5A, 13X, etc.) and natural zeolites absorb great amounts of water (0.2–0.3 g/g) in a narrow range at small values of the relative pressure P/P_0 (Fig. 3), which allows a high difference of temperature ΔT in the evaporator and condenser but, at the same time, requires a high temperature for regeneration (150–200°C). Silica gels, conversely, are easily regenerated (60°–100°C) but yield a small value of ΔT ; for this reason, they are often used in cascade cycles [35]. In this connection, it is necessary to search for new adsorbents for AdHE whose thermodynamic characteristics meet the requirements of a concrete cycle, in particular, working from a low potential source of heat.

The common approach to search for a solid adsorbent is enumeration of commercially accessible porous materials (see, for example, [36]). This choice is palliative, since the thus found adsorbent is the most optimal for the given cycle only among those materials that are in catalogs. The analysis shows [14, 37, 38] that, for different cycles, the requirements for the optimal adsorbent can be so different that the known adsorbents cannot provide the needed properties. More suitable can be another approach [37] based on that, for each concrete cycle, it is possible to first formulate the requirements for an ideal adsorbent optimal from the thermodynamical viewpoint just for the given cycle, then synthesize a real adsorbent whose properties will be close to the

properties of the optimal one. This approach will be discussed in more detail below.

2. NEW ASPECTS OF CHHE AND SHE APPLICATION IN LIGHT OF THE MONTREAL AND KYOTO PROTOCOLS

As was noted, the measures of the Montreal and Kyoto protocols can change the world's (and every country's) established balance of energy technologies; in particular, they can stimulate the development and use of ChHE and SHE. In [39], methods are developed allowing, with account for these measures, a comparative analysis of the environmental and economic aspects of the use of ChHE and SHE and of the present systems of heating and refrigeration. This approach, using generalized parameters such as the total yearly consumption of energy, the average value of the device efficiency, the average prices of energy, and others was used in [40] to account for the concrete conditions in Russia. Some results of this analysis follow.

Cooling systems. In the climate conditions of the RF and RB, the systems of sorption heating can be better than systems of sorption cooling. However, we will begin with the analysis of the latter, since, in this case, the analysis will be more general. Indeed, for refrigeration devices, there are two sources of GG: direct emission due to freon and indirect due to energy consumption. For measurement of the total GG emission, the following value [39] is introduced

$$E = MGWP\tau + WA. \quad (12)$$

Compare this characteristic for SHE

$$E_s = \frac{Q_0}{COP_s \eta_b} A_s \quad (13)$$

and for normal CHE

$$E_c = \frac{Q_0}{COP_c} A_{el} + MGWP\tau, \quad (14)$$

where the value A_s depends on the kind of supplied energy: $A_s = A_{n.g.}$; i.e., A_s equals the amount of CO_2 produced per 1 kW/h of heat obtained when burning natural gas, and $A_s = 0$ when using heat wastes. The cooling load Q_0 and the mass of the working liquid M are proportional to the power of cooling W_{cool} : $Q_0 = H'W_{cool}$ and $M = mW_{cool}$.

Now, consider two cases depending on the source of energy for regeneration:

1. CHE and natural gas. Combining equations (13) and (14), it is possible to write the relative decrease of the GG emission due to use of such a sorption heat engine:

$$\varepsilon = \frac{E_c - E_s}{E_s} = \beta \eta_b \frac{A_{el}}{A_{n.g.}} - 1 + \frac{m}{H} \frac{MGWP\tau}{A_{n.g.}} COP_s \eta_b, \quad (15)$$

where $\beta = \text{COP}_s / \text{COP}_c$. The negative value ε means that SHE with heating from natural gas is ecologically less pure than CHE. From (15), it is seen that ε depends not only on the characteristics of the device (COP , GWP , τ , m) but also on the time of its operation (H') and the method of generation of electric power (through the values A_{el} and $A_{\text{n.g.}}$). In most cases, the direct emission of freon can be ignored and expression (15) is simplified:

$$\varepsilon \approx \beta \eta_b \frac{A_{\text{el}}}{A_{\text{n.g}}} - 1.$$

Therefore, $\varepsilon > 1$ if $A_{\text{el}}/A_{\text{n.g}} > \frac{2}{\beta \eta_b}$ of $\beta \eta_b > \frac{2}{A_{\text{el}}} A_{\text{n.g}}$.

Compare SHE on the basis of the working pair $\text{LiBr-H}_2\text{O}$ with regeneration by burning natural gas ($A_{\text{n.g}} = 0.2 \text{ kg CO}_2/(\text{kW h})$, $\eta_b = 0.85$), which at this time has the highest efficiency ($\text{COP}_s = 1.2$), with an electric refrigerator. This analysis was made with the assumption that $H' = 1000 \text{ h/year}$ and $A_{\text{el}} = 0.65 \text{ kg CO}_2/(\text{kW h})$ (which agrees with the data for the RF). It has turned out that even such effective devices are environmentally cleaner when only compared with an average effective CHE with $\text{COP}_c \leq 3$ and only if it uses "dirty" freon R-404a ($\text{gwp} = 3800$). This means that, in most of the practical cases, the use of SHE deteriorates the situation with GG emission, the cause for which is indirect contribution of emissions (mainly CO_2) due to relatively low COP of SHE. If electric power is generated using atomic or hydroelectric power stations ($A_{\text{el}} \ll 0.65 \text{ kg CO}_2/(\text{kW h})$), the ecological advantage of CHE will be still higher, as in the introduction of quotas on the emission of CO_2 .

A similar approach can be used for the analysis of summary annual expenditures of carbon on generation of refrigeration (in the RF and RB) for both technologies. Thus, for SHE on the basis of natural gas,

$$C_s = \frac{Q_0}{\text{COP}_s} \left(\frac{k_{\text{n.g.}}}{\eta_b} + A_{\text{n.g}} q \right)$$

and, for SHE with an electric drive,

$$C_c = \frac{Q_0}{\text{COP}_c} (k_{\text{el}} + A_{\text{el}} q);$$

i.e., the economy per year will be

$$C = C_c - C_s = \frac{Q_0}{\text{COP}_c} \left(k_{\text{el}} + A_{\text{el}} q - \frac{k_{\text{n.g.}}}{\beta \eta_b} - A_{\text{n.g}} q \right). \quad (16)$$

The adsorption devices will be commercially more profitable than the compression ones if $C > 0$ or

$$k_{\text{el}} + A_{\text{el}} q > \frac{k_{\text{n.g.}}}{\beta \eta_b} + A_{\text{n.g}} q. \quad (17)$$

In the present situation when the tax on emissions is 0, the condition

$$\frac{k_{\text{el}}}{k_{\text{n.g.}}} > \frac{1}{\beta \eta_b} \quad (18)$$

must hold. Assuming $\eta_b = 0.85$ and $\beta = 0.3$, the relationship $k_{\text{el}}/k_{\text{n.g.}}$ will exceed 3.4. In accordance with the prices over all the recent years, this relationship in Russia was more than 6; i.e., SHE are commercially more profitable than compression heat pumps despite the higher GG emissions [40]. Similar conclusions were made in [41] in the analysis of the efficiency of thermodynamical cycles for heat stations.

In the introduction of a tax on emissions, the commercial advantage of adsorption systems will hold until the relationships

$$q \leq \left(k_{\text{el}} - \frac{k_{\text{n.g.}}}{\beta \eta_b} \right) / \left(\frac{A_{\text{n.g.}}}{\beta} - A_{\text{el}} \right) \quad (19)$$

hold. The equality $A_{\text{n.g.}}/\beta = A_{\text{el}}$ relates to the situation where the amount of CO_2 generated by SHE and CHE are equal. The commercial efficiency in this case is determined by relationship (17).

2. SHE with regeneration from heat emissions or solar energy. Such a device is always environmentally clean independent of its COP as it does not produce any GG. Then, the decrease of the emission of CO_2 is equal to the emission for the case of CHE and the yearly savings is determined by equation (18) in which $k_{\text{n.g.}} = A_{\text{n.g.}} = 0$. For a more detailed analysis, it is necessary to take into account the energy used for creation of the SHE itself and the associated emissions of CO_2 .

In sum, it is possible to conclude that SHE can be environmentally cleaner than CHE when "fed" from natural gas only in exceptional cases and always with the use of heat waste or solar energy. This is a constraint on the use of SHE, which, this notwithstanding, is of high interest in all cases where, for regeneration, it is possible to use commonly dissipated low potential heat, in the first case, for systems of air conditioning in cars and especially for systems of trigeneration (simultaneous generation of electric power, heat, and refrigeration).

Heating systems (ChHE and SHE). For heating systems more suitable for the climate conditions of Russia, Ukraine, and the RB, compare the emissions of CO_2 for a sorption heat pump (SHP) and a usual gas heater (GH), respectively:

$$E_s = \frac{Q_h}{\text{COA}_s \eta_b} A_{\text{n.g.}}, \quad (20)$$

$$E_b = \frac{Q_h}{\eta_b} A_{\text{n.g.}}. \quad (21)$$

Assuming that the source of primary energy is the same, find the decrease of emission ε :

$$\varepsilon = \frac{E_b - E_s}{E_b} = 1 - \frac{1}{\text{COA}_s}. \quad (22)$$

If $\text{COA}_s > 1$, we obtain decreased emissions. It can be appreciable, making up 41% at $\text{COA}_s = 1.7$ and 33% at $\text{COA}_s = 1.5$. For the cost of the consumed energy, we obtain

$$C_s = \frac{Q_h}{\text{COA}_s \eta_b} k_{n.g.}, \quad (23)$$

$$C_b = \frac{Q_h}{\eta_b} k_{n.g.}. \quad (24)$$

For the share of savings in this cost,

$$\gamma = \frac{C_b - C_s}{C_b} = 1 - \frac{1}{\text{COA}_s} = \varepsilon. \quad (25)$$

Therefore, at $\text{COA}_s > 1$, adsorption heat pumps are both environmentally cleaner and commercially more profitable than gas heaters. Their advantage is still more after the introduction of quotas on GG emissions. In this connection, it seems important to use targeted use of resources obtained from the sale of quotas for financing energy-saving projects, in particular, creation and development of ChHE and SHE production and markets. These can be absorption systems based on the pair LiBr–H₂O with $\text{COA}_s = 1.7$ (41% of the energy economy) or adsorption heat pumps based on the zeolite–water pair with two absorbers, which yields $\text{COA}_s \approx 1.5$ (33% savings). Of high interest can be adsorption heat pumps based on the pair selective sorbent of water (SSW)—water with two adsorbers—which theoretically can lead to $\text{COA}_s \approx 1.7$ at regeneration temperatures below 130°C [42, 43]. The latter allows, on the one hand, the use for regeneration of low potential heat (heat wastes, solar energy, etc.) and, on the other, the use of water instead of oil as the heat carrier. The use of heat wastes makes it possible to reduce the emissions of CO₂ down to null and obtain more resources from the sale of quotas.

3. THE PRESENT STATE OF SORPTION TECHNOLOGIES IN THE WORLD

It is known that a considerable part of the world population now needs heat pumps for heating and refrigeration [44, 45]. There are widely used electrically driven steam compression heat pumps where, instead of environmentally harmful coolant R22, safe coolants R410A and R407C [43] are used. Ecologically safe working liquids for compression heat pumps are also propane, propylene, ammonia, and CO₂.

In western countries, compression heat pumps have been used already for more than 30 years. Thus, in Sweden, they account for 50% of heating. By different esti-

mates, from 90 to 150 million units are used [44, 45] now in the world. Their yearly sales are \$125 billion, which is three times the world sales of arms. In Japan, about 3 million heat pumps are made per year. The USA produce about 1 million geothermal heat pumps, and, in the construction of new public buildings, use is predominantly of such pumps (this norm has been fixed by the Federal Legislature of the USA). The source of low temperature heat in about 75% of heat pumps installed in Europe is the outdoor air. The total volume of the production of heat pumps designed only for heating of the “water–air” class instead of gas and liquid-fueled boilers was in Europe 25 thousand pieces in 2002 and 35 thousand pieces in 2003. In Southern Europe (Italy, Spain, and Greece), systems of the “air–air” type and, in Northern Europe, heat pumps taking heat from the ground by in-depth coil heat exchangers prevail. By predictions of the World Energy Committee, by 2020, the share of heat pumps in heat supply will make up 75% [46].

A crucial precondition for active development of heat pump technology in the world is aid from the state. In many advanced countries, there are state foundations and programs stimulating energy saving for energy intensive enterprises. An example of such aid can be the practice of tax reduction accepted in Denmark (mostly through decreased tax components in tariffs for consumed energy resources) for enterprises having regular energy audits and continuous monitoring of energy consumption and performing all energy saving measures recommended by auditors with the payback time being below 4 years. Moreover, in this case, enterprises can expect state subsidies up to 30% of the expenditures on energy surveys. In Germany, the state bodies promote the perfection of heat pump units for heating premises and for domestic hot water production and promote their availability from a specialized sales network that provides installation [46].

The commercial production of absorption heat engines exists now mainly in Japan and the USA. Leaders in the market are the companies York, Trane, Carrier (USA), and Sanyo (Japan). In the recent 5–7 years, China (for example, the companies Broad, Shuangliang, Zhejiang, etc.) also has started the commercial production of AbHE for systems for air conditioning industrial enterprises (absorption heat pumps using the work pair bromine lithium–water). Interestingly, these companies using state support have the possibility to apply all of the most advanced technologies. By their turnover, they are leading manufacturers of absorption engines, and, to their own country alone, they have supplied over 20 thousand units of the equipment. The AbHE produced in different countries have a power of 0.1–5 MW. At the very recent time, absorption heat engines have appeared in the market that can be used in individual housing units and small communities. Their payback time is a little longer than that for large engines.

Adsorption technologies now only begin to appear in the market of energy saving technologies. A short time ago, only adsorption water chillers produced since 1986 by the Japanese company Nishiyodo Kuchouki Co. Ltd. on the basis of the work pair silica gel Fuij RD–water were commercially available [8, 47, 48]. The properties of this work pair allow the use for regeneration of heat with a temperature potential $T_g = 50\text{--}90^\circ\text{C}$ (for example, warm water from the cooling system of different engines). The minimal temperature of the adsorber is usually maintained at the level of 30°C . At $T_g = 90^\circ\text{C}$ and $T_e = 15^\circ\text{C}$, the cooling coefficient (COP) may reach 0.7. The manufacturer has evaluated the pay-back of these devices at two or three years. Another company making commercial adsorption refrigerators is Micon Co. Ltd. (Japan) [8]. In these devices, hot water is used at $T_g = 75^\circ\text{C}$ and cold water is generated at $T_e = 9^\circ\text{C}$ for air conditioning purposes, and the COP = 0.6. Both kinds of adsorption heat engines (AdHE) are sold in the markets of the USA, Canada, and Europe. Their typical power is 0.1–0.5 MW.

For individual housing, of high interest are adsorption heat pumps of low power. Prototype models of such devices with power of about 5–10 kW and over are being tested in China, Germany, Holland, Italy, Great Britain, Austria, Japan, Spain, and other countries [6, 7, 18, 30, 33, 49–56]. Recently, several European firms (SolarNext, Vaillant, SorTEch AG, etc.) have offered AdHE with power of 5–20 kW in which, for adsorbent heat regeneration, wastes with temperatures of 60–100°C, solar water and air heaters, or burning heat of natural gas are used. Such devices for utilization of the heat of car engines for compartment air conditioning are also actively developed [14, 15].

It should be noted that the use of sorption engines is especially suitable at the presence of comparatively cheap sources of heat of sorbent regeneration (steams of low and high pressure or liquid from the system of cooling of different engines, turbines, or technological processes; exhaust gases; etc.) It is important that the development of sorption refrigerators will be much stimulated by the future spread of the systems of cogeneration of energy (of sources of combined production of electric power and heat) and, accordingly, by creation of sources of trigeneration.

Another important factor of the SHE operation is low temperature source of heat which appreciably influences the design of the heat pump in commercial and environmental terms.

The main sources include [46, 57]: (1) ambient air; (2) exhaust air (ventilation emissions); (3) water of rivers and lakes; (4) ground and ground waters; (5) rocks.

Table 2 summarizes the sources temperatures from [46], as well as the medium of the intermediate loop for each of them.

Table 2. The values of the temperatures of different sources of low potential heat and data on the medium of the intermediate loop for them

Source	Medium of the intermediate loop	Temperature of source, °C
Ground waters	Water	8–15
Ground	Antifreeze	2–10
Water from the water supply point	Water	6–10
River water	Antifreeze	1–10
Sewer drains	Water	10–17
Ambient air	Air	from –10 to +15
Exhaust air	"	18–25

4. THE PRESENT STATE AND FEATURES OF APPLICATION OF SORPTION TECHNOLOGIES IN RUSSIA AND REPUBLIC OF BELARUS

The climate of the RF and RB is cooler than in the countries of West Europe, the USA and Japan, so about 25% of all energy costs go directly to heating [3]. This is achieved largely by burning organic fuels with appropriate emissions of GG to the atmosphere. In this connection a fairly high interest can be in the use of heat pumps for heating. In summer period there a certain niche also for systems of refrigeration (air conditioning, water cooling, storage of food). As was mentioned, production of cold is also of a high interest in systems of air conditioning in cars and, in particular, in devices of tri-generation, which are sources simultaneously of electric power, heat and cooling.

In the operation of a heat pump the ambient is used as “free of charge” source of low temperature heat (T_e), and in the operation of refrigerator for “dumping” of average temperature heat (T_c), i.e. some parameters of the cycle of sorption heat engine (SHE) are directly determined by climatic conditions. The analysis follows. In this connection consider briefly the features of the use of CHE and SHE in the climatic conditions of the RF and RB.

The Republic of Belarus is situated in the geographic zone where average temperature in summer period exceeds 20°C and in winter is close to 0°C . Adsorption reverse heat pumps designed at the ITMO of the NAS of Belarus allows production from 20 to 30 kW/m³ of heat energy and up to 5 kW of refrigeration. Such pumps save up to 15–20% of primary energy (of fuel) to generation of electricity, heat and cooling (Fig. 4). The incidence in Europe of such energy facilities will yield the economy of energy up to 50×10^{12} kJ per year, which equals 1.6×10^9 m³ of natural gas (300 million euro). In this case the emission of carbonic acid to environment will be 3×10^7 t less.

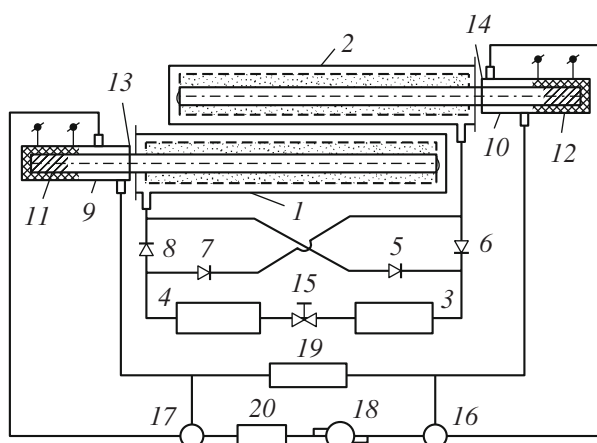


Fig. 4. Scheme of adsorption heat pump: 1, 2—adsorbers filled with sorbent; 3—condenser; 4—evaporator; 5–8—valves; 9, 10—liquid heat exchangers; 11, 12—heaters; 13, 14—heat pipes; 15—adjustable throttle; 16, 17—triple valves; 18—liquid pump; 19—rotameter, 20—thermostat.

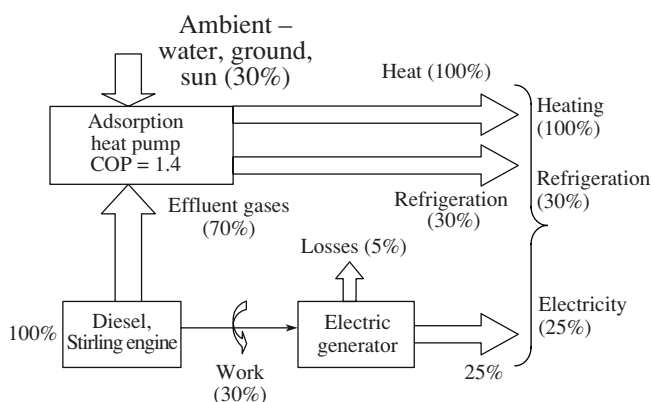


Fig. 5 Scheme of the sorption heat engine in the trigeneration system (electricity, heat, cooling).

Adsorption heat engines are also of interest to use them in transport. Within the fifth framework program (EU F5 Energie program) in the European Community a SOCOOL project has been recently made that is oriented to creation of tri-generation energy systems used for domestic needs. An increase by 15–20% in the efficiency of such facilities is due to utilization of heat of effluent gases and discharge liquor of the diesel generators or Stirling engines to produce cooling with attraction of sorption technologies (Fig. 5). Sorption heat pumps and refrigerators of a new type are to be cheap, reliable, long-term and have a high thermodynamical efficiency. In order to achieve this purpose it is needed to intensify the process of heat- and mass exchange in porous sorbent and the heat exchange of sorbent with the wall of the adsorber and the ambient. In orientation to the use of diesel-generator units it is possible to utilize the heat of both effluent gases and cooling liquor. Good prospects for utilization of the released heat in

modern fuel elements (especially high temperature ones) make it possible to expect the wide spread of these elements instead of steam turbines and electric generators on heat electric stations. To achieve this purpose, sorption technologies of high pressure (activated coal/ammonia) and in orientation to heat of the cooling liquor the technologies of low pressure (silica gel/water) are used. Sorption technologies are noiseless because of the absence of mechanical compressor. No environmentally harmful coolants (CFC, HCFC, HFC) are used in them. As was mentioned above, sorption refrigerators on solid sorbents with refrigerating capacity over 100 kW have been developed and commercially available.

At the Institute of Heat and Mass Exchange of the NAS of Belarus new miniature refrigerating engines and heat pumps have been developed that are of interest for the use in the countryside. Similar works are being done in the European community within the SOCOOL project. Fig. 6 presents a sorption heat pump of 4 kW designed to heat air and refrigerate water.

It consists of four adsorbers filled with sorbent composite (micro crystals CaCl_2 on the surface of the active coal fiber). The evaporator of the heat pump is used to cool water and the condenser of the pump and finned adsorbers to heat air in premises.

Scientific and technological basis of the design of the heat pump is based on innovation solution: choice of an effective pair sorbent/sorbate, intensification of the processes of heat- and mass exchange inside sorbent and the sorbent with the wall of adsorber, increased specific capacity of sorbent, etc. To provide long-time life resource of the heat pump a number of problems have to be solved that include compatibility of materials and heat carriers and guarantee of absence of non-condensing gases inside the cooling engine. To achieve the high density of the stored energy and thermodynamics efficiency of the heat pump, the sorbent has to be very cheap, nontoxic, not inflammable, ecologically clean and to have a high heat of sorption. As a sorbent, preference is given to activated coals, silica gels, zeolites, salts of metals and the composites of these materials. Typical samples of coal sorbents and composites (micro crystals of the salt on fiber) are shown in Fig. 7.

The source of heat energy for the pump presented in Fig. 8 is a gas burner (or motor-generator effluent gases) and as a low temperature source of energy the reverse water of the heating system is used. In the use of gas burner, the heating of adsorbers and desorption of sorbent take place. Simultaneously, spent gases heat water in the heat exchanger-reclaimer from 6 to 50–60°C, then 5 kW of heat energy are generated. Bypass gas flaps allow organization of the cooling-heating cycle of adsorbers due to periodic feed alternately now cold air, now hot gases from the burner (internal combustion engine). Cold and hot gases are necessary for adsorption-desorption of sorbent in adsorbers. Due to



Fig. 6. Sorption heat pump for heating air and cooling water of the ITMO NAS Belarus design; power 4 kW in heating 1 kW in cooling.

the work of adsorbers water cooling is achieved in the liquid circulation loop to temperature 3–5°C and 1 kW of cooling is produced. Such a unit is suitable for cooling milk on dairies.

Figure 9 shows the view and structure of the sorption heat pump containing six adsorbers with summary power in heat of 3.6 kW with external and internal regeneration. Due to this the efficiency of the pump (COP) attains 1.62, and its efficiency in cooling generation is 0.6.

For further increasing the efficiency of heat pumps on solid and liquid sorbents and their adaptation to high temperature heat engines it is reasonable to use the so called two/three cascade thermodynamical cycles. For example, the utilization of dumped heat of high temperature fuel elements it is easy to make with the help of adsorption heat pumps coupled sequentially with low temperature adsorption heat pumps (LiBr–water). The temperature of the off-heat gas (600–800°C) of the heat engine is lowered to 300–400°C. Gas is fed to the average temperature adsorber (NiCl_2) and again the process of desorption of the working substance proceeds. In the end, the cooled gas gets into the low temperature absorber containing the LiBr–water pair where water vapors are desorbed from the brine. Figure 10 gives the scheme of the tricascade heat pump and Clapeyron–Clausius diagram for it.

Sorption solar refrigerators. Solar refrigerator is a kind of the heat pump on solid sorbents, in the evaporator of which temperature below the ambient temperature is maintained. Sorption technologies provide economy of energy and environment protection in creation of refrigerators with the use of alternative sources of energy, first of all solar energy [52, 53].

Figure 11 presents the scheme of the refrigerator on solid sorbents with the use of short cycles of operation (20–30 minutes) developed at the ITMO NAS of Belarus, where the solar energy is used for generation of refrigeration and heat. In daytime this process is car-

ried out with the help of solar energy, and at night for generation of refrigeration electric power is used. The solar refrigerator can heat water (1 kW of heat) and cool the air in the freezing room (200 kW of refrigeration). The refrigerator consists of two adsorbers filled with sorbent, and a system of thermal regulation on heat pipes. The solar energy heats the evaporator of the heat pipe, and the heated steam alternatively is used for desorption of one of the adsorbers. In heat pipes the working liquor is water in average temperature loop

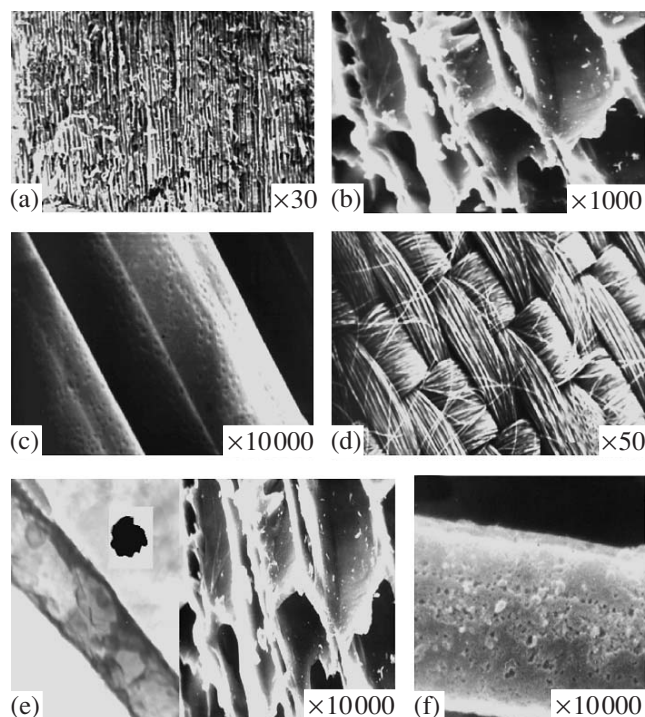


Fig. 7. Sample of the coal sorbent (a, b—activated wood coal, c, d—activated coal fiber) and the sorbent composite (e, f) for the heat pump.

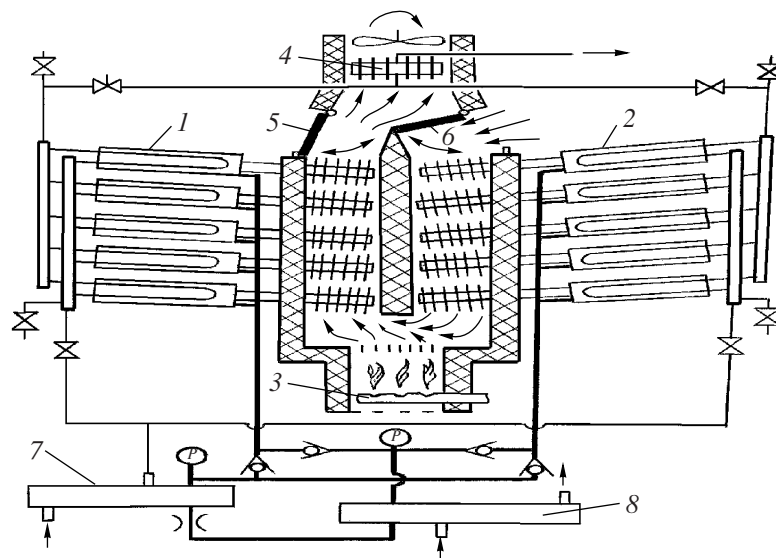


Fig. 8. Scheme of the sorption heat pump of the ITMO NAS Belarus design for production of overheated steam and hot and cool water (5–10°C): 1, 2—adsorbers; 3—gas burner; 4—boiler; 5, 6—bypass gas flaps; 7—evaporator; 8—condenser.

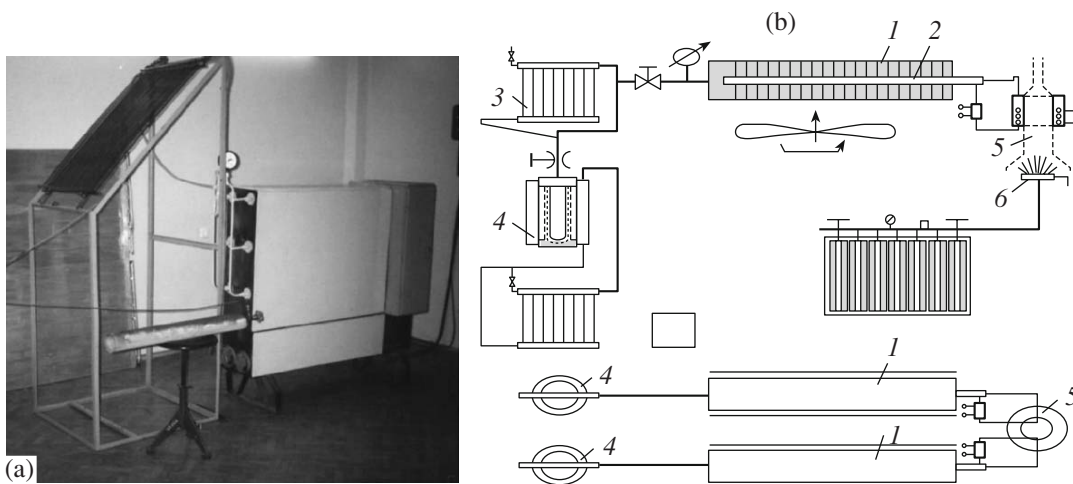


Fig. 9. External view (a) and scheme (b) of the sorption bicyclical heat engine: 1, 2—adsorbers; 3—condenser; 4—evaporator; 5—heat pipe; 6—gas burner.

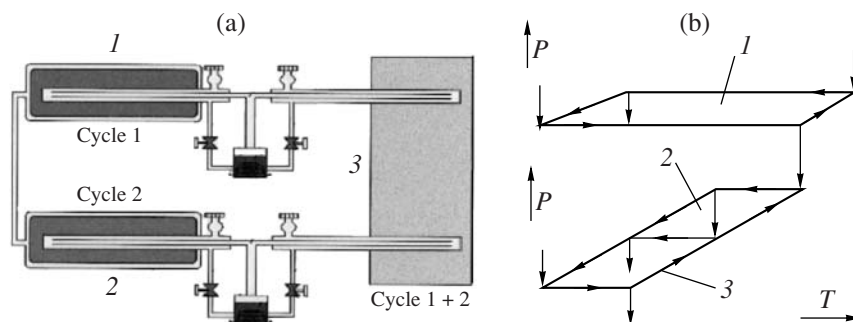


Fig. 10. Scheme (a) and Clapeyron–Clausius diagram (b) of the tricascade sorption heat pump with internal regeneration: 1—high temperature adsorber; 2—average temperature one; 3—low temperature (LiBr–water).

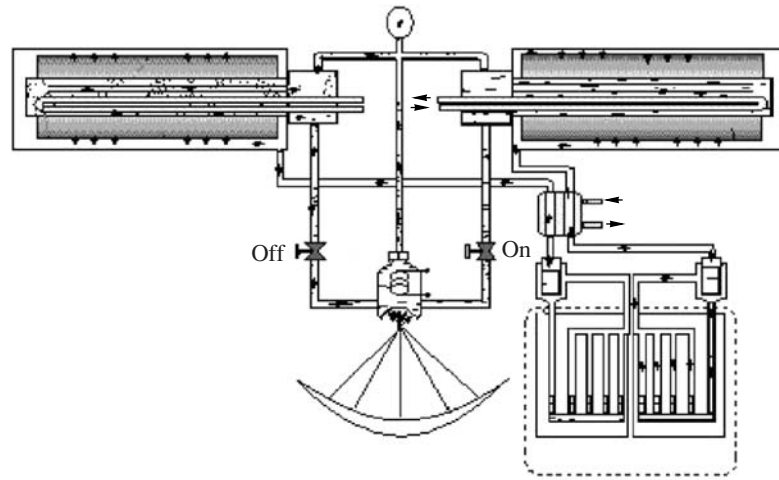


Fig. 11. Scheme of the sorption refrigerator working on solar and electric energy with the concentrator of solar radiation.

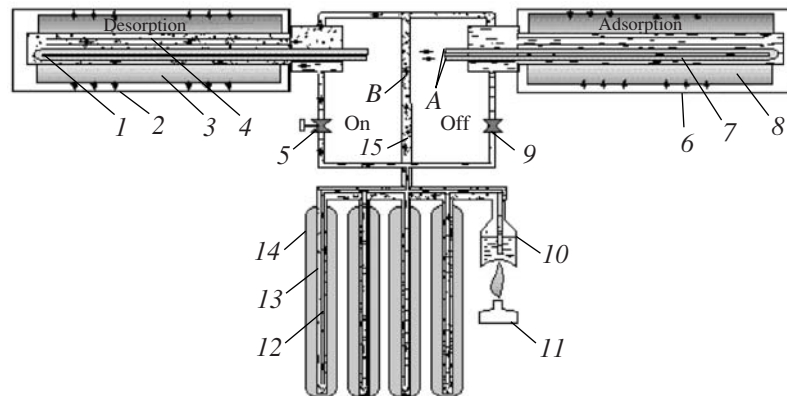


Fig. 12. Scheme of a two-adsorber solar refrigerator with vacuum vessels—receivers of diffuse solar radiation: 1, 7—heat exchangers; 2, 6—adsorbers; 3, 8—sorbent; 4—steam channel inside the sorbent; 5, 9—liquor heat exchangers; 10, 13—evaporators of the thermal siphon; 11—gas burner; 12—liquor channel of the thermal siphon; 14—vacuum vessel; 15—steam channel; A—entry of cooling liquor; B—steam flow from the evaporator to the condenser.

and ammonia in low temperature one. The system of thermal regulation on heat pipes makes it possible to avoid mechanical pumps. The weight of the refrigerator does not exceed 20 kg.

Figure 12 shows the scheme of the second prototype of the solar refrigerator where as an alternative to solar source of energy a miniature gas burner is used. The basic components of such a refrigerator are solar collector (concentrator), vessels with sorbent, evaporator and condenser.

A substantial component of the solar refrigerator is also a two-phase system of thermal regulation providing generation of cooling round the clock. In this case there is no need to wait for night for cooling the freezing room. In the result, the masses of sorbent and body of adsorbers can be considerably decreased comparing to the refrigerators of the day/night type. Two modifications of the solar refrigerator have been developed. The first refrigerator has a solar concentrator in

the focus of which the evaporator of the steam-dynamic thermal siphon is constantly present. The second design is based on the use of glass collectors-accumulators of solar radiation that are commercially available. Inside the collector there is an evaporator of the thermal siphon, receiving solar energy from the local solar concentrator placed in the vessel. The design of the solar refrigerator is good for operation and allows using different amounts of vacuum vessels according to the value of heat load. The unique feature of the refrigerator is the design of the system of thermal regulation (thermal siphon system with collectors/evaporators and collectors/concentrators) and valves for change-over of the liquor flow from condensers to the evaporator. The system of the thermal regulation is used for periodic heat and cooling of vessels with sorbent.

A more continental climate is characteristics of the European part of Russia where the most of the country's population live. In northern and eastern areas of

the RF the average temperature in winter may fall to $-30\ldots-50^{\circ}\text{C}$. Under the conditions of cold winter the air, as a rule, cannot be used as the low temperature source of heat, and the heat exchanger is to be placed in the ground deeper than in a milder climate. It is profitable to use heat of natural water reservoirs and ground waters. Thus, in Western Siberia, due to geothermal waters the temperature of the evaporator can be increased up to $20\text{--}30^{\circ}\text{C}$.

Under conditions of cold climate it is preferable to select as the working body (sorbate) a liquid with a high pressure of steam, i.e. ammonia and methanol. For systems of cooling and conditioning in summer time it is most profitable to use water.

As was already noted, at present in Russia about a quarter of energy costs go to heating domestic and industrial premises. In this connection the use of SHE in this sector of the economy can be the most profitable both in terms of economy and ecology. Excessive energy resources are spent also in the Russian industry where the energy intensity is $1/3$ above that in Canada, about double the level of the USA, Sweden and Finland and 3–4 times that in other countries of West Europe and Japan.

In Russia only about 150 heat pumps are used with summary power of 75 MW, while in the world the number of such facilities is about million fold. At the same time, it is possible to speak about the availability of resources of low potential heat that could be transformed by the heat pumps (HP). Consider basic sources of heat for them:

(1) It is first of all waste heat appearing in the system of heat supply. By estimation of L.A. Ogurechnikov, the waste heat of industrial enterprises of oil refinement, chemical industry and ferrous metallurgy is equivalent to 100–150 million tons of equivalent fuel per year [58]. Under centralized production of heat at a level of 1470 million Gcal (the 2001 data), its losses in heat loops and in consumers make up to 40–50% (by 20% in loops and in consumers according to the data of Energy Strategy) which equals 590–735 million Gcal or 80–105 million tons equivalent fuel. Half of all centrally produced heat is consumed in utilities with appropriate losses of 40–55 million tons of equivalent fuel. A large part of these losses are likely to be utilized by heat pumps at comparatively high values of the energy conversion factor.

(2) Disposed heat of the heat energy facilities. In the scheme of the development of heating cogeneration heat pumps get an economic niche for direct accumulation of heat from the reverse loop water in the faraway consumer on the price of released heat. This becomes an alternative to construction of expensive heat loops in the center of heat loads of large cities. Thus, for the situation of the city of Omsk, in the result of the use of released energy from heat electric power plant in the installation of adsorption heat pumps it is possible per each 1 Gcal (of end consumption) to save 0.22 tons of

equivalent fuel [58]. Due to utilization of heat of outgoing gases with the help of heat pumps per 1 Gcal at the end consumer it is possible to save 0.014 tons of equivalent fuel consumed by heat energy facilities.

The potential of natural sources of high temperature heat for heat pumps is very difficult to measure but it is obvious that it is very large. Thus, the potential of only geothermal sources of Russia is 3450 PJ/g, or 118 million tons of equivalent fuel [58]. At the same time one should bear in mind that in most cases (maybe except for the use of the sources of geothermal heat) the coefficients of the energy conversion for natural sources of heat will be lower than for the released heat of the domestic sector and production.

The estimations show that up to 20% of heat losses in systems of district heat supply of the housing and utilities can be used for transformation by heat pumps. For evaluation, the heat pumps with the power already achieved in practice were taken, i.e. absorption lithium bromide ones developed at the Teplosibmash open-end company [58] in which instead of the heating medium or fuel, gas and steam are used, and steam compression heat pumps developed at Energia closed-end company [58] and working on electric power or gas. The advantages of absorption systems are determined first of all by that they are operating in stationary mode and there is no need in alternative cooling and heating the sorbent. Note that AbHE on steam as environmentally cleaner can become even more profitable commercially under the appropriate system of fines for GG emissions.

At the Institute of Thermal Physics of the SB RAS trial-commercial steam compression heat pumps of new generation have been created for production of hot water in the heating systems and hot water supply ($55\text{--}80^{\circ}\text{C}$) with simultaneous production of moderate cooling ($2\text{--}10^{\circ}\text{C}$) for systems of conditioning and cooling of various technological media (Fig. 13). If needed, these engines can be used as refrigeration ones. The development was awarded Great Gold Medal of the Siberian Fair in the nomination "Energy- and Resource Saving." Start was given to production of heat pumps with heat capacity from 30 to 1000 kW. The designing of heat pump facilities, manufacturing, delivery, installation, start-up and setting works and service maintenance are carried out by the OOO SKB IPI on the commercial basis of individual orders.

Commercial absorption lithium-bromide heat pumps and cooling engines of the new generation for heating and cooling of water and of other media (Fig. 14). In these engines the metal intensity, dimensions were made substantially lower, and the life time increased (minimum 20 years). The commercial production of engines of different type-sizes have been started:

cooling engines for cooling of water from 6°C and over on various kinds of warming sources (steam, hot water, fuel) with refrigerating capacity from 250 to 5000 kW;

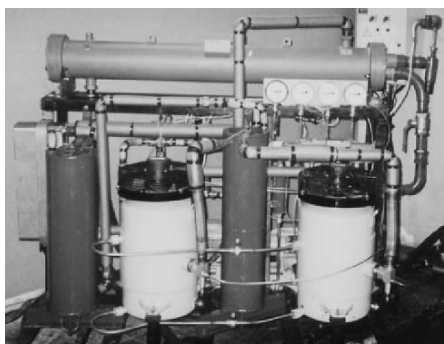


Fig. 13. Pilot commercial steam compression heat pump of hot water in heating systems with simultaneous production of refrigeration.



Fig. 14. Absorption heat engines generated in the OOO OKB Teplosibmach.

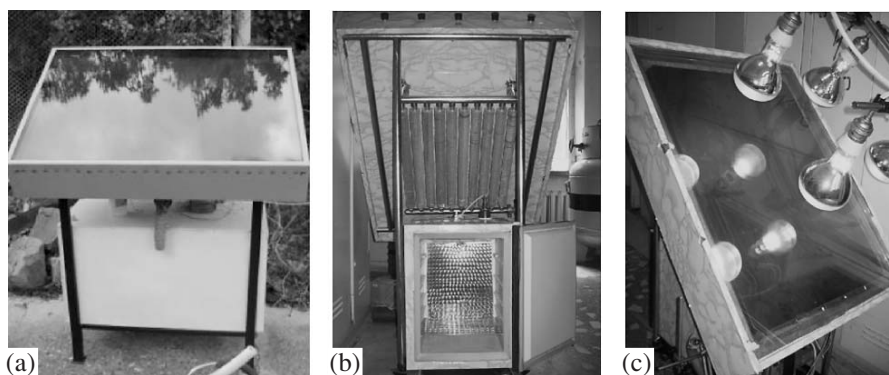


Fig. 15. Solar adsorption refrigerators according to [59] (a) and [60] (b—cooling room and condenser; c—heating by electric lamps).

heat pumps for heating water up to 55–80°C with the use of released low potential heat (20–40°C) and various kinds of heating sources with heat capacity from 500 to 5000 kW.

The delivery of engines and engineering support is carried out by the Teplosibmach on the commercial basis for individual orders.

Heat pumps of compression type, or thermal transformers, are ecological clean compact freon facilities allowing production of heat for heating and hot water supply due to use of the heat of a low potential source. As such a source use can be made of: industrial and purified domestic drains; heat of thermal waters; heat produced in purification of smoke gases, etc. The cost of heat produced by heat engines (depending on the work efficiency) is 1.6–3.7 times as low as with district heating.

Within the framework of the international project INTAS 03-51-6260 “Solar Assisted Adsorption Chiller Using New Adsorbent Materials” (with participation of research team IK SB RAS, OIBT RAS, MGU, ITT NAN of the Ukraine, ITAE-CNR, RWTH-Aachen) a solar adsorption refrigerator [59] was designed and successfully tested in the Crimea in 2006 (Fig. 15a). In this

device as a working liquid water was used and as adsorbent the composite CCB-1K (silica gel modified by the calcium chloride), described below in more detail. The analogue created at the IC SB RAS is tested both under solar illumination and in heating by electric incandescent lamps (Fig. 15b). The latter mode allows the creation of regulated conditions of heating and the comparison among, for example, different adsorbents [60]. The device has an area of beam receiving surface of 0.7 m², has about 20 kg of adsorbent and is characterized by solar chilling coefficient of 0.18–0.21 [59]. The solar adsorption refrigerator on the work pair ammonia—calcium chloride has been produced at the Astrakhan State University and described in [61, 62].

The above analysis shows substantial lagging of the RF and RB in production and utilization of heat pumps for heating and cooling. At present the level of HE development in these countries is substantially behind the world level, and this makes it necessary to take serious and immediate measures liquidate this lagging behind and seems really possible since in the RF and RB a high research-engineering potential in the field of the research of heat engines of ab- and adsorption types has been accumulated. One of the results of this is development and manufacturing in Russia of lithium

Table 3. Characteristics of lithium-bromide absorption heat engines

Parameters	Piston pump	Screw pump		
	HT-300	HT-500	HT-1000	HT-3000
Heating power, kW:				
for water 8°C	300	500	1000	2500
for water 25°C	400	800	1600	4000
Power of the consumed electric energy, kW h:				
for water 8°C	90	150	300	630
Aggregate dimensions, m:				
compressor	4.5 × 1.8 × 1.7	2.8 × 2.2 × 1.1	4.0 × 1.5 × 2.3	5.2 × 2.0 × 3.0
condenser–evaporator		3.9 × 2.7 × 1.7	4.9 × 2.1 × 1.5	5.0 × 1.7 × 3.3
Mass, kg	4300	9700	15000	22000

bromide absorption heat engines and refrigerators with power of 0.6–11 MW (see Table 3). For the RB conditions schemes of heat supply of individual houses by use of SHE have been designed.

5. NEW WORK PAIRS FOR ADSORPTION HEAT ENGINES. ADSORBENT IS ONE OF THE BASIC COMPONENTS OF ADHE AND TO A HIGH DEGREE DETERMINES ITS OUTPUT CHARACTERISTICS

The effect of properties of adsorbents on AdHE parameters. Criteria for choice of adsorbent optimal for a concrete cycle of AdHE. An essential problem in the development of efficient AdHE is the choice of adsorbent allowing production of optimal operation characteristics, the most important of which are the chilling COP and specific cooling heat over the cycle Q_{cool} . As was mentioned, the COP value directly determines also the environmental cleanness of the AdHE. The question of the choice of adsorbent optimal for a concrete adsorption cycle without heat regeneration is considered in [37, 38, 63, 64] where only thermodynamical analysis of the requirements to the optimal

adsorbent is made, while some kinetic aspects are discussed in [60, 65].

Consider an ideal cycle of adsorption refrigerator (AdR) using the Clapeyron-Clausius diagram (see Fig. 2b). As was noted, the cycle is entirely determined by three temperatures: of the heat carrier in condenser T_c and evaporator T_e , as well as dehydration of adsorbent $T_3 = T_g$. In case all three temperatures of the cycle are given, the efficiency of AdR (COP) is monotonously increasing with increased amount of the working liquid exchanged in the cycle Δw , asymptotically tending to $\Delta H_{evap}/\Delta H_{desorp}$ which is schematically shown in Fig. 16 [63]. The specific heat of cooling over the cycle $Q_{cool} = \Delta H_{evap}\Delta w$ with increase of Δw is increasing still quicker. Therefore, to increase the COP and Q_{cool} it is necessary to use adsorbent having greater different Δw between extreme isosters of the cycle 1–2 and 3–4 in Fig. 2. On the basis of this simple criterion in [63, 64], a procedure has been developed that allows a preliminary selection of material promising for adsorption cooling by sorption characteristics. It is based on the principle of the Polanyi temperature invariance [65], according to which at different temperatures of T' and T'' the same degree of adsorption space filling with adsorbate is achieved at vapor pressures P' and P'' related to each other as

$$T' \ln \frac{P'}{P_s} = T'' \ln \frac{P''}{P_s}. \quad (26)$$

From this principle the mutually one-to-one relationship follows between the value of adsorption and the adsorption potential $\Delta F = -RT \ln \frac{P}{P_s} \ln p$ which was

later used by M.M. Dubinin in the theory of volume filling of micropores [66, 67]. In this case the volume of adsorbed working liquid if the function of only one variable (ΔF), but not usual two (temperature and pressure), which appreciably simplifies the analysis. It has turned out that the Polanyi principle of temperature invariance is fairly universal, so it is possible to use it

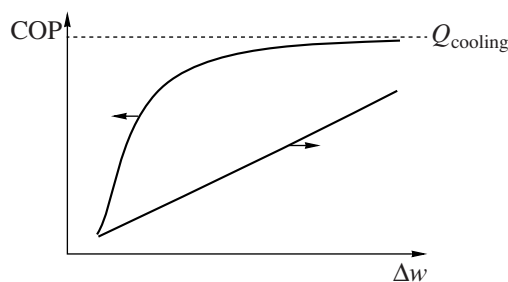


Fig. 16. Dependence of the COP and the specific power of the adsorption refrigerator on the specific amount of water exchanged in the cycle (the dotted line is the asymptotic value of $\Delta H_{evap}/\Delta H_{desorp}$).

for many adsorbents of both micro- and mesoporous nature [68].

If this principle holds, then to the left extreme isotherm of the cycle 1–2 for which the adsorption is maximum (w_{\max}), the adsorption potential $\Delta F_{\min}(T_e, T_c) = -RT \ln P(T_e)/P_s(T_c)$ is relevant. In Table 4 both the values of the adsorption potential $\Delta F_{\min}(T_e, T_c)$ and the values $\Delta F_{\max}(T_c, T_g)$ are given for the extreme right isotherm with the minimum adsorption at $T_e = 278$ K, $T_c = 303$ K, $T_g = 353$ K. It is reasonable to apply this approach to the search for optimal adsorbent among the already known materials satisfying the Polanyi principle. It is possible to use the data available in literature about adsorption properties, including those obtained at temperatures and pressure different from those realized in the real cycle of adsorption and absorption chemical heat engines (ACE). In particular, this analysis can be based only on one isotherm or isobar of adsorption. It is only important that the experimental data comply with the range of the values $\Delta F_{\min} \leq \Delta F \leq \Delta F_{\max}$. In [63, 64] this approach is successfully applied to the choice of adsorbents of water and methanol for adsorption refrigerator, the motive power of which is low potential heat.

Consider now a case where for the cycle AdHE given are only temperatures T_e and T_c and determine the minimum temperature $T_{\min} = T_d = T_2$ (Fig. 2) required for isobaric desorption of working liquid if over the sorbent the pressure P_c is held. It is obvious that for adsorbent satisfying the Polanyi principle this temperature cannot be calculated from the equality $\Delta F(T_e, T_c) = \Delta F(T_c, T_{\min})$. Another approach is application of the Truton empirical rule by which the isosters of the sorption of working liquid and the curve of its equilibrium with the vapor are intersected at $T \Rightarrow \infty$ [2, 69, 70]. This statement deviates from the formulation of the Truton rule accepted in chemistry by which the molal entropy of evaporation of any liquid is equal to about 89 J/(mol K) [9]. Our analysis has shown that the empirical rule holds for most of working pairs used in AdHE: water–silica gel Fuji Davison RD, water–zeolite 13X, water–composites “salt in porous matrix”, CO_2 –coal, methanol–coal (AC-35, TA90), methanol–hydrophobic zeolite CBV 901 Y and ammonia–coal PX31, as well as for basic working pairs AbHE: ammoni–water, water–LiBr and methanol–LiBr.

For the case where this rule holds it is easy to produce the universal relationship between three temperatures providing the reversibility of the cycle:

$$T_c^2 = T_e T_g, \quad (27)$$

which does not depend on the nature of adsorbent and adsorbate. Note that in [12] this relationship was obtained from the conditions of cycle reversibility of the ideal absorption heat engine without consideration of the detailed kind of dependence $P(T)$. Table 5 gives experimental ($T_{2\text{exp}}$) and calculated from (27) ($T_{2\text{cal}}$) temperature for the work pair methanol–coal TA90 and

Table 4. Values of the adsorption potential relevant to the minimum and maximum adsorption

Operating liquid	$\Delta F_{\min}(T_e, T_c)$, J/mol	$\Delta F_{\max}(T_e, T_c)$, J/mol
Water	3991.3	7072.5
Methane	3470.5	6225.4
Ammonia	2057.6	3717.8

Table 5. Experimental and calculated temperatures for the working pair methanol–coal TA90

T_e , °C	T_c , °C	$T_{2\text{exp}}$, °C	$T_{2\text{cal}}$, °C	ΔT , °C
0	26.3	56.1	55.1	–1.0
0	30.6	63.0	64.6	1.6
0	36.1	77.2	77.0	–0.2
0	41.5	90.1	89.3	–0.8
0	50.1	110.5	109.4	–1.1
10	37.1	66.3	66.8	0.5
10	41.0	76.8	75.4	–1.4
10	46.5	87.2	87.7	0.5
10	51.7	102.3	101.2	–1.1

their difference ΔT . It is seen that the latter is equal to 1–2°C, which is close to the accuracy of finding $T_{2\text{exp}}$.

From (13) several useful conclusions follow. Thus, the minimum temperature of desorption for cycles of cooling and heating can be calculated like in [12, 69, 70]

$$T_{\min} = \frac{T_c^2}{T_e}. \quad (28)$$

The external source of heat which is used for desorption, obviously, should have temperature $T_g \geq T_{\min}$. If $T_g < T_{\min}$, then the process cannot be realized, since the pressure over sorbent cannot attain the pressure in condenser P_c . At $T_g = T_{\min}$ the process will be reversible, and the efficiency of AdHE maximum:

$$\text{COP}_{\max} = \left(\frac{1}{T_c} - \frac{1}{T_g} \right) / \left(\frac{1}{T_e} - \frac{1}{T_c} \right).$$

If $T_g > T_c$, the efficiency decreases, since heat is transmitted at the end difference of temperature between adsorber and external source of heat. Therefore, *optimal adsorbent* should keep at pressure P_c the maximum mass of the working liquid at $T < T_{\min}$ and at the achievement of the temperature T_{\min} all of it should be removed. So for such an adsorbent the isobar of desorption at P_c should be step-wise (Fig. 17, curves 1) like for systems with monovariant type of equilibrium [37, 38]. For real adsorbent the equilibrium is divariant, so maximum amount of working liquid has to be exchanged in a narrow range of temperatures close to T_{\min} (Fig. 17,

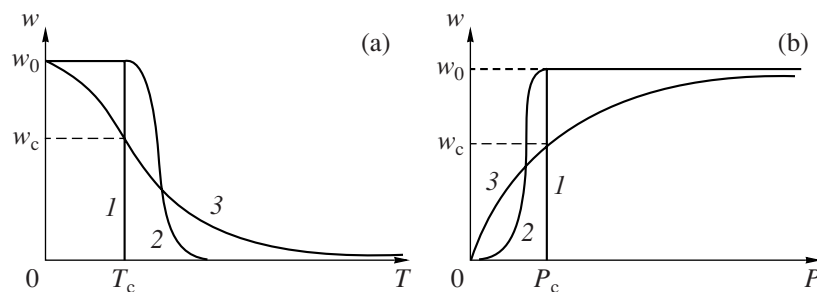


Fig. 17. Typical isobars $P = P_c = \text{const}$ (a) and isotherms $T = T_c = \text{const}$ (b) of adsorption in the case of mono- (1) and divariant (2, 3) equilibrium.

curves 2). It is obvious that adsorbents CCB-1K, FAM-Z02, CCB-5K and FAM-Z01 comply with the isotherms are represented in Fig. 3.

Figure 18 presents dependences $T_{\min}(T_c)$ calculated from (28) for three different modes of cooling: air conditioning ($T_e = 10^\circ\text{C}$), generation of ice ($T_e = -5^\circ\text{C}$) and deep freezing ($T_e = -30^\circ\text{C}$). Consider some examples in detail.

Air conditioning. One of the most demanded application of adsorption and absorption heat engines is air conditioning in the car compartment [14, 15]. In the evaporator it is necessary to keep temperature $T_e = 7$ – 12°C and the temperature of condenser is $T_c = 35$ – 45°C . The relationship (28) allows estimation of minimum temperature required for regeneration of the adsorbent. For the most hard conditions ($T_e = 7^\circ\text{C}$, $T_c = 45^\circ\text{C}$) $T_{\min} = 88^\circ\text{C}$ and for soft ($T_e = 12^\circ\text{C}$, $T_c = 35^\circ\text{C}$) $T_{\min} = 60^\circ\text{C}$. In the second case for regeneration of adsorbent it is possible to use the heat from the system of engine cooling since its temperature potential T_g is usually above 80°C [14, 15]. The first of the mentioned modes also can be realized with this heat but it is rather difficult because its temperature potential is

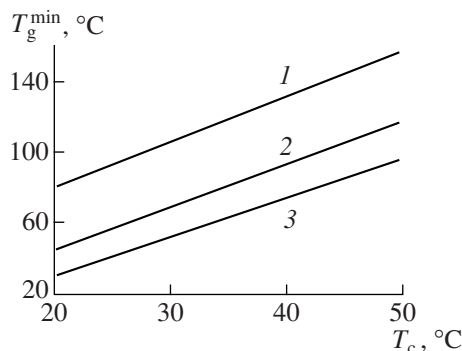


Fig. 18. Minimum temperature of the external source of heat T_g^{\min} depending on the temperature of the condenser for three variants of adsorption cooling: deep freezing (1), production of ice (2), and air conditioning (3).

below 95°C and difference of 7°C can be not enough to provide the required power of conditioning.

Air conditioning in premises is easier: even in hot climate ($T_c = 45$ – 50°C) in order to produce $T_e = 10^\circ\text{C}$, minimum regeneration temperature of 84 – 95°C is needed that is achievable by rather simple and cheap solar energy (SE) collectors [59, 71] or heat of cooling different engines [8, 14, 15] that is usually dissipated.

Production of ice. In hot climate ($T_c = 45$ – 50°C) to produce ice ($T_e = 0^\circ\text{C}$) it is needed a source of heat with minimum temperature 100 – 110°C , which it is more difficult to make in simple SE collectors. For this purpose, selective coatings or vacuum insulation [71] is needed which makes the collector much more expensive. In moderate climate ($T_c = 30^\circ\text{C}$) $T_g \geq 63^\circ\text{C}$, which it is quite attainable under conditions of solar radiation, typical, for example, of the middle zone of Russia in summer. Note that in solar adsorption refrigerators the regeneration is to be made by day, and refrigeration by night, at lower temperature of adsorber equal to ambient temperature. This makes it possible to produce also a lower temperature in the evaporator. This example of daily provision of heat is examined in more detail below. The round clock production of refrigeration is possible by use of solar refrigerators developed at the Institute of Heat and Mass Exchange of the National Academy of Sciences of Belarus [84–86]. The original system of thermoregulation makes it possible to carry out recirculation of refrigerating fluid during the short time of the cycle (20–30 min).

Deep freezing. In order to cool the evaporator to temperature $T_e = -18^\circ\text{C}$ that is recommended for deep freezing provided the condenser is at $T_c = 2^\circ\text{C}$ it is needed to make regeneration of adsorbent at a temperature exceeding 64°C . Even at $T_e = -50^\circ\text{C}$ the minimum temperature of regeneration remains rather easily attainable: $T_g \geq 112^\circ\text{C}$. This shows that the adsorption devices can be efficient and obtain comparatively low temperatures required, for example for storage of vaccines or drying thermolabile substances [34]. Potential AdHE (ChHE) for these purposes has not been so far realized.

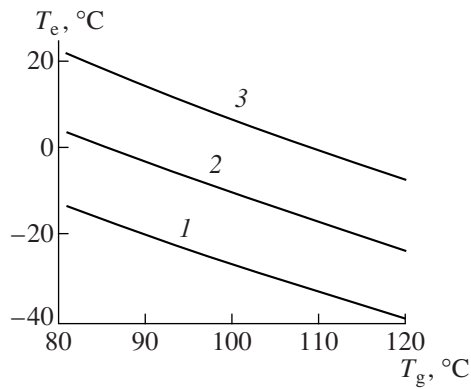


Fig. 19. The relationship of the temperature of the evaporator to the temperature of the external source at different temperatures of the condenser: 1— $T_c = 30$; 2—40; 3—50°C.

In this connection it is of interest to appreciate the minimum temperature T_e^{\min} which can be obtained in the evaporator if for regeneration a source of heat with temperature T_g is accessible, and the temperature of the condenser is equal to T_c . From the universal equation (27) it follows that

$$T_e^{\min} = \frac{T_c^2}{T_g}. \quad (29)$$

Thus, having the heat source with $T_g = 80^\circ\text{C}$, in cool climate ($T_c = 20^\circ\text{C}$) it is possible to obtain $T_e = -30^\circ\text{C}$, and in hot climate ($T_c = 45^\circ\text{C}$) in all $+13^\circ\text{C}$, i.e., the effect of condenser (adsorber) temperature is important. Figure 19 presents the relationship $T_e(T_g)$ under three rather high values of T_c calculated by equation (29). It is seen, for example, that the temperature recommended for freezing -18°C is attainable even at the ambient temperature $T_c = 30^\circ\text{C}$ when regeneration of adsorbent occurs only at 87°C . In particular, if for solar adsorption refrigerator by day (at the stage of regeneration) it was managed to heat the adsorbent to the temperature T_g , then at night at the adsorbent temperature T_c equal to the ambient temperature (which is lower than

by day), it will be possible to obtain in the evaporator also much lower temperature $T_e^{\min}(\text{night})$ than in the realization of the cooling stage by day: $T_e^{\min}(\text{day}) = T_c^2(\text{day})/T_g > T_e^{\min}(\text{night}) = T_c^2(\text{night})/T_g$. Thus, at $T_g = 67^\circ\text{C}$ $T_c(\text{day}) = 30^\circ\text{C}$ and $T_c(\text{night}) = 16^\circ\text{C}$ we obtain $T_e^{\min}(\text{night}) = -29^\circ\text{C} \ll -3^\circ\text{C} = T_e^{\min}(\text{day})$. In Fig. 20a the relationship $T_e(T_c)$ is calculated by equation (29). From the figure it is seen that even at not high temperature of regeneration it is possible in principle to attain in the evaporator the temperature below -20°C if the adsorber and condenser are kept at a temperature not above $+20^\circ\text{C}$.

The universal relationship (27) makes it possible to estimate also the maximum temperature T_c^{\max} which is attainable in the condenser (at the desorption stage) and in adsorber (at the stage of adsorption) if the temperature of the external source of heat T_g and of evaporator T_e are given:

$$T_c = \sqrt{T_g T_e}. \quad (30)$$

This estimation is of interest for analysis of ecologically clean and energetically efficient adsorption heaters. Thus, in the use of a water body with a temperature of 5°C as the evaporator and consumption for regeneration of sorbent of heat Q at temperature $70\text{--}80^\circ\text{C}$ in the condenser and adsorber, it is possible to produce heat $(1.5\text{--}1.8)Q$ at temperature $35\text{--}40^\circ\text{C}$, which is quite enough for heating, for example, of floor in domestic and office premises. If for evaporation ground water with temperature $20\text{--}25^\circ\text{C}$ are used (reserves of this natural source of heat are huge in many areas of Russia), it is possible to obtain heat with the temperature potential $45\text{--}50^\circ\text{C}$. Calculated by (30) relationships $T_c(T_e)$ at different T_g are presented in Fig. 20b.

If the stage of adsorbent regeneration is performed in summer using solar energy and thereby store it, then at the stage of adsorption in winter it is possible to get in the adsorber this stored energy at temperature $T_c \leq T_c^{\max}$.

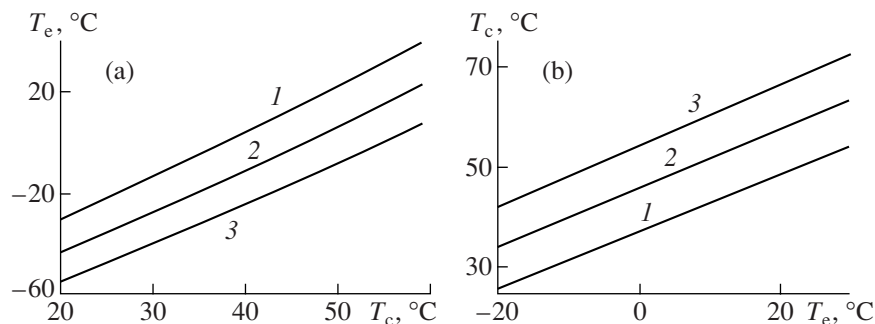


Fig. 20. Relationship of the evaporator temperature to the condenser temperature (a) and of the condenser temperature to the evaporator temperature (b) at different temperatures of the external source: $T_g = (1) 120^\circ\text{C}$; (2) 100°C , and (3) 80°C .

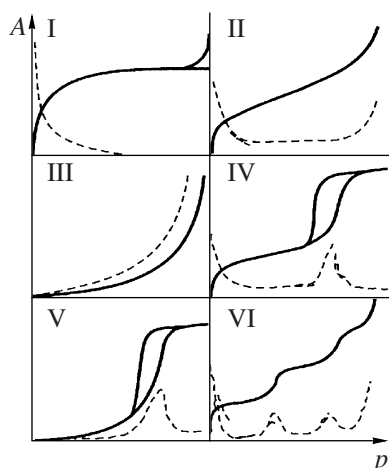


Fig. 21. Isotherms of adsorption (bold lines) and their derivatives (dashed lines): I–VI—different types of isotherms according to [73, 74].

In this case the heat pump operates as a device for storing the heat energy, making the full cycle during the year. For countries where the difference of price of “daily” and “night” electricity is high (for example, Japan [71]), ChHE (ATM) can be applied to create the reserve of “cheap” electricity at night in order to use the stored heat by day. In this case it is possible to obtain a high value of T_c^{\max} since the electrical heater makes it possible to attain high values of regeneration temperature T_g . Thus, at $T_g = 300^\circ\text{C}$ and $T_e = 5^\circ\text{C}$ $T_c^{\max} = 126^\circ\text{C}$. In this process one should use reaction proceeding at high temperatures, for example $\text{MgO} + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2$, or adsorbents with high temperature of regeneration, for example, zeolites.

So the universal relationship (27) allows formulating the requirement to the adsorbent optimal for a concrete cycle AdHE (without heat regeneration) in the given climate zone. Thus, Fig. 18 shows that to produce ice, for example, in the hot climate ($T_c = 45^\circ\text{C}$) a heat source with $T_g \geq 105^\circ$ is needed, while in the cool climate ($T_c = 20^\circ\text{C}$) it is enough to have a heat source with $T_g \geq 47^\circ\text{C}$. In the former case adsorbent is needed which maintains the temperature of working liquid up to 105°C and then releases heat in a narrow range of temperatures at $T \geq 105^\circ\text{C}$, and in the latter the process proceeds at a much lower temperature.

In this connection it is of interest to analyze the applicability of known types of adsorbents in AdHE. For this, we use classification which was first suggested in [73] by which most of isotherms of adsorption can be related to one of five types (I–V). Besides, we have examined comparatively scarcely occurring step-wise isotherms which in [74] are related to type VI. All these isotherms are presented in Fig. 21. It has turned out, that promising materials in the systems of adsorption cooling can be those which are capable in a relatively

narrow range of change of adsorption potential ΔF (or relative pressure $p = P/P_0$) to reversely sorbate/desorbate a great amount of working liquid w . So the derivative $dw/d(\Delta F)$ or dw/dp for these adsorbents should be high in the required range of values ΔF or p . This criterion is met by adsorbents with isotherms of type I, IV, V and VI.

Theoretically, ideal are the step-wise isotherms of type VI which for usual one-component adsorbents can be obtained only in exotic cases. For realization of such isotherms it is suggested to modify common sorbents by inorganic salts [37, 38]. The change of the value of sorption is at the expense of the progress of the chemical reaction between the working liquid and salt with formation of crystal solvates of salt, the equilibrium of which is monovariant. It is such adsorbents that are examined below.

Development of methods of targeted synthesis of composite adsorbents of water for adsorption heat engines. Since maximum large amount of working liquid is exchanged in a narrow temperature range close to T_{\min} as sorbents, it is best of all to use solid substances the equilibrium of which with working liquid is monovariant, as, for example, in reaction (1) of gas-solid type. Indeed, it is ChHE that in principle allow the attainment of maximum efficiency in a simple cycle without regeneration of heat [13]. So inorganic salts can be more promising than usual adsorbents with divariant type of equilibrium. Temperatures of decomposition of complexes of some salts with water at pressure of 56.3 mbar (which is appropriate to $T_c = 35^\circ\text{C}$) are presented in Table 6. It is seen, that for the considered hydrates the temperature of decomposition is changing from 37 to 155°C , so that for any temperature potential of the external source of heat it is possible to select the appropriate hydrate. A similar situation is observed for ammoniates [75]. For reactions of salt with lower alcohols the thermodynamical data are very scarce [76, 77], by which theoretical selection of salt is impossible and so enumeration has to be done [64].

Despite the noted advantages of ChHE with massive salts, their practical application is impeded by several serious factors:

- (a) substantial increase of the volume of solid phase in the course of the formation of the complex (for complexes with ammonia it may reach 3 or 4 fold) [17, 22, 78];
- (b) hysteresis in reaction (1), in the result of which decomposition of the complex may proceed at a much higher temperature than its formation [79–81];
- (c) small speed of reaction (1) due to undeveloped reaction surface and/or formation at the salt surface of a new phase through which gas diffusion is made difficult [81, 82];
- (d) corrosion activity of salts and complexes in contact with metal parts of ChHE.

To overcome these difficulties, as well as to improve the heat transference new two-component sorbets of ammonia [83–93], water [37, 38, 41, 79, 94–106] and methanol [64, 107] were suggested in which the micro crystals of active salt were placed at external or internal surface of a less activity component—matrix that served also as a dispersing agent, as well as facilitating improved heat and mass transfer in the sorbent layer. The arrangement of micro and nanoparticles of salts of metal on the surface of active coal fibers “salt on the surface of fiber” substantially stimulates the process of heat- and mass exchange, increases penetrability of the system, accelerates the process of gas filtration through sorbent and improves sorption capacity of the composite [109]. Cycles of sorption/desorption of the working liquid in heat engines are accelerated. Sorption of the working liquid by such materials proceeds largely due to reaction with salt like in ChHE, mechanization of the process is like in AdHE. Two-component adsorbents of “salt in porous matrix” and “salt on the surface of the fiber” types yield far more capabilities for varying their properties than one-component ones. In fact, for the latter it is possible to vary only the chemical nature of the adsorbent (silica gel, oxide of aluminum, zeolites, etc.) and its porous structure. For composites additionally it is possible to vary the chemical nature and method of application of the second component, as well as the relationship of the components.

The review of composite adsorbents of ammonia and water has been made recently in [108]. The basic conclusion can be summed in the following way:

(a) placement of salt in the pores of the matrix or at the surface of the active coal fiber provides the capability to solve the above mentioned problems of matrix from busofit, vermiculite and ACF make it possible “to smooth” large change in the volume of salt in chemical reaction [92, 109], hysteresis “synthesis-decomposition” can be removed or appreciably decrease [79], rate of hydration of disperse salt is determined by mass transfer and not by chemical reaction [109–112], encapsulation of salt in pores prevents from its contact with the walls and removes corrosion;

(b) adsorption of water by composite is not linear superposition of adsorption with salt and matrix, i.e., synergism of properties [79] is observed. In particular, pressure (and, therefore, the temperature) of the reaction (1) can be shifted placing salt in the pores of matrix. Thus, the temperature of the formation of hydrates and methanolates increases with decreased size of pores [37, 79] (Table 6), and for formation of ammonia complexes [92] this effect diminishes. This effect makes it possible “close fitting” of the temperature of transfer (reaction (1)) to that which is required by a concrete cycle;

(c) salt in pores forms two phases – volumetric crystalline and superficial X-ray amorphous which qualitatively differ by character of water absorption. Sorption equilibrium of composite sorbents with vapors of water

Table 6. Values of the temperature T_d appropriate for transitions between different hydrates of salt in mass and dispersion (pores sizes of 15 nm) states at a water vapor pressure of 56.3 bar

Salt	Transition	$T_d, ^\circ\text{C}$	
		mass state	dispersion state
Na_2SO_4	1 \rightarrow 7	39	46
	7 \rightarrow 10	37	–
Na_2HPO_4	0 \rightarrow 2	53–55	–
	2 \rightarrow 7	45–49	–
$\text{Ca}(\text{NO}_3)_2$	0 \rightarrow 2	65–67	70–72
MgSO_4	0 \rightarrow 1	114	210–270
	1 \rightarrow 2	99–101	155–210
	2 \rightarrow 4	71–75	–
	4 \rightarrow 6	59–63	–
CaCl_2	0 \rightarrow 1/3	>155	–
	1/3 \rightarrow 2	104–108	110–115
	2 \rightarrow 4	71–73	76–80
LiBr	0 \rightarrow 1	155	155
	1 \rightarrow 2	104–108	115–135
LiCl	0 \rightarrow 1	80–87	76–80
	1 \rightarrow 2	100–105	87–98

depends on the relationship of crystalline and amorphous phases which it is possible to vary in the process of synthesis by changing the content of salt, pH of the impregnating solution and temperature of composite calcinations [100–103].

At present in the practical realization of heat engines on solid sorbents there has appeared a new direction associated with the systems of tri-generation of energy (electricity, heat, coolant) [112, 113]. The use of sorption heat engines together with internal or external combustion engines (diesel, Stirling engine) or with fuel elements of stationary use allows substantial increase of COP in the use of fuel and protection of natural environment.

CONCLUSIONS

(1) Application of SHE and CHE in the RF and RB provides high opportunities of energy saving in the power engineering, industry and utilities. The basic heat sources for these heat engines is heat of burning the natural gas, dumped heat of enterprises and systems of heat supply, as well as geothermal and ground waters. As a source of low temperature heat in the evaporator heat of the ambient and exhaust air, soil, natural water bodies, ground waters, sewage drains, etc., are used.

(2) At present the HP level of development in these countries is lagging behind the world level: thus, in the

RF there are about 150 HP comparing to 150 million in the world. Required are serious and swift measures to liquidate this backwardness.

(3) ChHE and SHE are preferential comparing to CHE because they do not use electric power. Their advantages can increase in the result of Russia's signing the Kyoto Protocol. For this reason it is important to use a target-oriented use of resources received from sale of quotas to greenhouse gases emissions to finance the energy saving projects, in particular, for the development of production and market of ChHE and SHE.

(4) In the climate conditions of the Russian Federation and Republic of Belarus the highest interest is in the use of HE for heating. The systems of sorption cooling can find application in summer time, including by use of solar energy as the source of heat with a high potential.

(5) In the RF and RB there has been accumulated serious scientific-technological potential in the field of the HP of sorption type, as well as intensification of heat- and mass transfer by means of heat pipes. A new family of composite adsorbents of water, ammonia and methanol have been developed for the systems of air conditioning.

(6) On the basis of the accumulated knowledge and experience the prototypes of adsorption systems for air conditioning and production of ice have been developed and tested. Production of new composite adsorbents for ChHE has been organized. For the RB conditions schemes of heat supply of individual housing units by use of SHE have been developed.

Since in the nearest time in the heat-power engineering of the RF and RB substantial restructuring is needed requiring considerable investments, part of the resources it would be reasonable to direct to introduction of the existing heat pump technologies (including vapor compression ones) and creation of new heat engines of chemical and sorption type.

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NOTATIONS

A —amount of CO_2 generated per 1 kW/h of energy consumed by the device; A_s , A_{el} , $A_{n.g.}$ —amount of CO_2 for SHE in generation of electric power when using natural gas; C_s , C_c , C_b —summary annual expenditure (cost) of consumed energy for SHE, CHE, and gas boilers; COA_s —gain factor for SHE; COP—refrigerating coefficient; COP_s , COP_c —refrigerating coefficients for SHE and CHE; E —volume of GG emitted to the atmosphere; ΔF —adsorption potential; GWP—global warming potential; H' —time of the operation of the

device; H —enthalpy; ΔH —heat of the formation of SV; ΔH^0 and ΔS^0 —changes of the standard enthalpy and entropy in formation of SV; ΔH_e and ΔS_e —changes of enthalpy and entropy in evaporation; ΔH_{evap} and ΔS_{des} —the heat of evaporation and desorption; k_{el} and $k_{n.g.}$ —cost of 1 kW/h of electricity and the heat produced by burning the natural gas; M —mass of the working liquid; m —mass of the sorbent; P —pressure; P_0 —fixed pressure; P_s —pressure of saturated vapors of the adsorbate; P_c —equilibrium pressure in the condenser; $p = P/P_0$; Q —heat; Q_h —heat release per year; Q_0 —average per year cooling load; Q_{cool} —specific heat of refrigeration per cycle; q —tax on emission of 1 kg of CO_2 to the atmosphere; R —universal gas constant; S —entropy; T —temperature; T_1 , T_2 , T_3 —temperatures appropriate for positions 1, 2, and 3 in Fig. 2; T_g , T_c , and T_e —temperatures of the external source, condenser, and evaporator; T_d —temperature of desorption; V —volume of sorbent; W —power; W_{sp} —specific power; W' —energy consumption per year; W_{cool} —cooling power; w —ratio of the mass of the adsorbed gas to the mass of the sorbent; Δw —amount of working liquid exchanged in the cycle; ε —relative decrease of GG emission; γ —saved share of the cost of the consumed energy; η —efficiency of the heat engine; η_{cool} —cooling coefficient; η_{heat} —heat gain factor; $\eta_{t.p.}$ —factor of the temperature potential change; η_b —efficiency of heat production in the combustion chamber; τ —yearly leak of working liquid.

Indices

b—boiler; c—condenser; cal—calculated; d—desorption; e—evaporator; el—electric energy; exp—experimental; g—external source (gas); h—heat release; max—maximal; min—minimal; n.g.—natural gas; s—sorption; des—desorption; evap—evaporation; heat—heating; cool—cooling; t.p.—temperature potential, sp—specific.

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